DESCRIPTION

METHOD FOR PRODUCING UPGRADED COAL FOR USE IN METALLURGY AND

METHOD FOR PRODUCING REDUCED METAL AND SLAG CONTAINING

OXIDIZED NONFERROUS METAL USING THE COAL

Technical Field

The present invention relates to the field of a
technology for producing a reduced metal such as reduced
iron and a slag containing an oxidized nonferrous metal
using coal as a reducing agent. More specifically, the
present invention relates to a method for upgrading low-rank
coal such as high-volatile coal, and a method for producing
a reduced metal and a slag containing an oxidized nonferrous
metal using the upgraded coal.

Background Art

A coal-based direct reduction process used as an
alternative to a blast furnace process is a process (so-
called carbon composite method) in which iron oxide
agglomerates incorporated with a carbonaceous material are
heated by radiation in a rotary hearth furnace to produce
reduced iron, and this process has already successfully been
brought into practical application on a commercial scale.
However, this process has the problem that the strength of
the agglomerates and heat transmission in the agglomerates

are insufficient depending on the properties of the coal used as the reducing agent, thereby influencing the properties of a reduced iron product.

The inventors of the present invention improved the above-mentioned carbon composite method to develop a method in which iron oxide agglomerates incorporated with a carbonaceous material are heated by radiation in a rotary hearth furnace to produce reduced iron, and then the reduced iron is melted by further heating at a high temperature to separate between a metal and a slag and recover the metal. Also, practical application of this method on a commercial scale has been advanced. However, this process has the problem that the metal and the slag cannot be sufficiently separated depending on the properties of the coal used as the reducing agent, and thus the metal remains in the slag, thereby decreasing the recovery yield of the metal.

In the field of conventional nonferrous metallurgy, as a method for producing a titanium oxide-containing slag by separating an iron component from a material, for example, an ilmenite ore containing titanium oxide and iron oxide, a method is used, in which the ilmenite ore is supplied to an electric furnace together with a carbonaceous reducing agent so that iron oxide is reduced, melted, and then taken out as melted iron, and a titanium oxide-containing slag is recovered as an intermediate product for a titanium refining

raw material. However, in this method, the temperature in the furnace is decreased by proceeding of reduction reaction of iron oxide, which is endothermic reaction, and thus much electric power is consumed for maintaining the temperature in the furnace. Also, the method has the problem that a large amount of melted FeO is produced in the treatment process, and thus the refractory in the furnace is greatly damaged by the melted FeO. Therefore, it is difficult to effectively produce a titanium oxide-containing slag using an electric furnace. There is further the problem that the inside of the furnace must be maintained in a highly reducing atmosphere for reducing iron oxide, and thus titanium oxide is also reduced by the highly reducing atmosphere.

Accordingly, the inventors of the present invention have advanced research and development for practical application of the above-described method disclosed by the inventors in consideration that as an alternative to the electric furnace method, the method can be basically applied to production of a slag containing an oxidized nonferrous metal, which is an intermediate product for nonferrous metallurgy. This method basically requires no electric power and does not damage the refractory because melted FeO is not produced. However, there still remains the problem that the ash in the coal used is mixed in the slag as in the

above-described electric furnace method, thereby decreasing
the product's value. There is further the problem that the
metal and the slag are not sufficiently separated depending
on the properties of the coal used as the reducing agent,
and thus metallic iron is mixed in the slag to decrease the
content of an oxidized nonferrous metal in the slag, thereby
further decreasing the product's value.

On the other hand, an attempt has been made to upgrade
low-rank coal such as high-volatile coal by solvent
treatment to produce a carbonaceous material for metallurgy.
When high-volatile coal without thermal plasticity is
treated in a solvent at about 400°C, the coal is separated
into an extract with the solvent and a residue. The extract
is known to have thermal plasticity which is absent from the
original coal. Also, it is indicated that high-strength
coke usable for a blast furnace and a cupola can be produced
using a mixture of the extract and the original coal or the
like.

Since the conventional method for upgrading coal with a
solvent is intended to be used in a vertical furnace such as
a blast furnace or the like, a carbonaceous material is
required to have load strength, and an operation of
expressing a caking property other than thermal plasticity
must be added. Furthermore, the conventional coal upgrading
method uses, as the solvent, a hydrogen donor substance such

as tetralin or the like for increasing the coal dissolving
power, or a nitrogen-containing solvent such as N-
methylpyrrolidinone or coal tar, and thus the method is
disadvantageous to industrial production for the following
reasons:

Since the hydrogen donor solvent loses its hydrogen
donating property in extraction, the solvent must be re-
hydrogenated for recycling the solvent. However, hydrogen
is very expensive, and there has been found substantially no
example of commercial application in the field of
metallurgical use. The nitrogen-containing solvent has
excessively high compatibility with coal, and thus the
solvent and the extracted coal are bonded together, thereby
failing to recover the solvent. This causes the problem of
failing to recycle the solvent.

The present invention has been achieved in
consideration of the above-described problems, and an object
of the invention is to provide a method for upgrading low-
rank coal such as high-volatile coal, which is unsuitable
for the conventional carbon composite method, to produce
upgraded coal for metallurgy which is suitable for the
carbon composite method. Another object of the present
invention is to provide a method for producing a high-
quality reduced metal and a slag containing an oxidized
nonferrous metal using the upgraded coal for metallurgy.

Disclosure of Invention

In an aspect of the present invention, a method for producing upgraded coal for metallurgy by extracting coal with an organic solvent comprises:

a slurry preparing step of mixing the coal and the organic solvent to prepare a raw material slurry;

an extraction step of aging the raw material slurry by heating to extract a soluble component of the coal with the organic solvent and prepare an extracted slurry; and

a solvent removing step of removing the organic solvent by evaporation from the extracted slurry to produce upgraded coal for metallurgy as a solid form.

In the present invention, the solvent removing step preferably comprises:

a sedimentation step of sedimenting the insoluble component of the coal by allowing the extracted slurry to stand to separate between a supernatant containing an extracted coal, i.e., the extracted soluble component, and a residual coal slurry containing a residual coal, i.e., the sedimented insoluble component; and

a first solvent removing step of removing the organic solvent by evaporation from the supernatant to produce the extracted coal as the upgraded coal for metallurgy.

Alternatively, the solvent removing step preferably

comprises:

a sedimentation step of sedimenting the insoluble component of the coal by allowing the extracted slurry to stand to separate between a supernatant containing an extracted coal, i.e., the extracted soluble component, and a residual coal slurry containing a residual coal, i.e., the sedimented insoluble component;

a first solvent removing step of removing the organic solvent by evaporation from the supernatant to produce the extracted coal as a solid form; and

a second solvent removing step of removing the organic solvent by evaporation from the residual coal slurry to produce the residual coal as a solid form.

The production method of the present invention preferably further comprises the following step:

a compounding step of compounding the extracted coal and the residual coal to produce the upgraded coal for metallurgy having controlled thermal plasticity.

The compounding ratio of the residual coal to the upgraded coal for metallurgy is preferably 0% by mass to 70% by mass. In the extraction step, the heating temperature is preferably 250°C to 400°C, and the aging time is preferably 5 to 120 minutes. In the extraction step, aging is preferably performed in a nitrogen atmosphere at 0.5 MPa or more.

The organic solvent used in carrying out the method of the present invention preferably contains a two ring aromatic compound as a main component and has a boiling point of 200°C to 300°C at normal pressure. This method preferably further comprises a solvent recovering step of recovering the organic solvent removed by evaporation and recycling it to the slurry preparing step. The recovered organic solvent is substantially not rehydrogenated. As preferred means for recovering the organic solvent, vacuum distillation or spray drying can be used.

The present invention further includes, as a subject of protection, the upgraded coal for metallurgy produced by the above-described method.

In another aspect of the present invention, a method for producing a reduced metal using the upgraded coal for metallurgy produced by extracting coal with an organic solvent comprises:

a coal upgrading step of aging the coal by heating in the organic solvent to produce upgraded coal for metallurgy having higher thermal plasticity than that of the coal;

a mixing step of mixing the upgraded coal for metallurgy and a metal oxide raw material containing a metal oxide to prepare a mixture; and

a reduction step of reducing the mixture by heating in a moving hearth furnace to produce a reduced metal as a

reduced mixture.

The production method of the present invention preferably further comprises the following step:

1) a step of successively heating the reduced mixture in the moving hearth furnace to agglomerate the reduced metal in the reduced mixture;

2) a melting step of melting the reduced mixture by heating in a melting furnace to separate between a metal and a slag, and a recovering step of discharging the metal to the outside of the furnace and recovering the metal as the reduced metal;

3) a reduction and melting step of reducing the mixture by heating in the moving hearth furnace to produce the reduced mixture, and then melting the reduced mixture by further heating to produce the reduced metal as a reduced melt; or

4) a reduction and melting step of reducing the mixture by heating in the moving hearth furnace to produce the reduced mixture, and then melting the reduced mixture by further heating to produce the reduced metal as a reduced melt, a solidification step of solidifying the reduced melt by cooling in the moving hearth furnace to produce a reduced solid, and a separation and recovery step of discharging the reduced solid to the outside of the furnace to separate between a metal and a slag and recover the metal as the

reduced metal.

In a further aspect of the present invention, a method for producing a slag containing an oxidized nonferrous metal using upgraded coal for metallurgy, which is produced by extracting coal with an organic solvent, comprises:

a coal upgrading step of aging the coal by heating in the organic solvent to produce the upgraded coal for metallurgy which has higher thermal plasticity than that of the coal;

a mixing step of mixing the upgraded coal for metallurgy and a metal oxide raw material containing iron oxide and an oxidized nonferrous metal to prepare a mixture;

a reduction and melting step of reducing the iron oxide in the mixture by heating the mixture in a moving hearth furnace to produce a reduced mixture containing metallic iron, and then melting the metallic iron by heating the reduced mixture to separate between the metallic iron and an oxidized nonferrous metal slag;

a solidification step of solidifying the mixture containing the oxidized nonferrous metal slag and the melted metallic iron by cooling in the moving hearth furnace to produce a reduced solid; and

a separation and recovery step of discharging the reduced solid to the outside of the furnace to separate between a metal and a slag and recover the slag as the

oxidized nonferrous metal slag.

The present invention further includes, as a subject of protection, the reduced metal and the oxidized nonferrous metal slag produced by the above-described methods.

Brief Description of the Drawings

Fig. 1 is a process flow diagram illustrating a method for producing upgraded coal for metallurgy according to an embodiment of the present invention, Fig. 2 is a process flow diagram illustrating a method for producing upgraded coal for metallurgy according to another embodiment of the present invention, and Fig. 3 is a process flow diagram according to a still another embodiment of the present invention.

Fig. 4 is a flow diagram illustrating a step of reducing a chromium-containing raw material in a method for producing a reduced metal by a carbon composite method using upgraded coal for metallurgy according to a further embodiment of the present invention, Fig. 5 is a flow diagram illustrating a step of reducing a chromium-containing raw material in a method for producing a reduced metal by a carbon composite method using upgraded coal for metallurgy according to a further embodiment of the present invention, and Fig. 6 is a flow diagram illustrating a step of reducing a titanium-containing raw material in a method

for producing a slag containing an oxidized nonferrous metal
by a carbon composite method using upgraded coal for
metallurgy according to a further embodiment of the present
invention.

Fig. 7 is a graph showing the relation between the
extraction temperature and the extraction rate of coal, Fig.
8 is a graph showing the relation between the extraction
time and the coal extraction rate, and Fig. 9 is a graph
showing the relation between the number of repeated uses of
a solvent and the coal extraction rate.

1 ... coal (original coal), 2 ... organic solvent, 3 ...
slurry preparing tank, 4 ... raw material slurry, 5 ...
slurry pump, 6 ... heat exchanger, 7 ... heater, 8 ... aging
tank, 9 ... sedimentation tank, 12, 13 ... solvent removing
apparatus (solvent recovering apparatus), 14 ... extracted
coal, 16 ... circulated solvent, 17 ... residual coal, 24 ...
solvent pump, 25 ... treated slurry, 26 ... supernatant,
27 ... residual coal slurry, 32 ... upgraded coal for
metallurgy (mixture), 101, 111 ... metal oxide-containing
raw material, 102, 112 ... upgraded coal for metallurgy, 103,
113 ... agglomerator, 104, 114 ... agglomerate (raw material
mixture or mixture), 105, 115, moving hearth furnace, 106 ...
reduced agglomerate (reduced mixture), 107 ... melting
furnace, 108, 118 ... metal, 109, 119 ... slag, 116 ...
reduced solid, 117 ... screen, 211 ... titanium-containing

raw material, 212 ... upgraded coal for metallurgy, 213 ...
agglomerator, 214 ... agglomerate (mixture), 215 ... moving
hearth furnace, 216 ... reduced solids, 217 ... screen,
218 ... metal, 219 ... slag

Best Mode for Carrying Out the Invention

Embodiments of the present invention will be described
in detail below with reference to the drawings.

[First Embodiment]

Fig. 1 shows an example of a process flow of a method
for producing upgraded coal for metallurgy according to an
embodiment of the present invention. As coal (original
coal) 1 used as a raw material, low-rank coal having no or
low thermal plasticity, such as bituminous coal, anthracite
coal, sub-bituminous coal, or lignite, can be used.

[Slurry preparing step]: First, the coal 1 and an organic
solvent (simply referred to as a "solvent" hereinafter) 2
are mixed in a slurry preparing tank 3 to prepare a raw
material slurry 4.

[Extraction step]: The raw material slurry 4 is transferred
to a heater 7 with a slurry pump 5 and heated therein. The
heating temperature is 250°C to 400°C and preferably 350°C
to 420°C. In order to decrease a heat load on the heater 7,
a heat exchanger 6 is preferably provided upstream the
heater 7, for pre-heating the raw material slurry 4 using
the latent heat of a circulated solvent 16 which will be

described below.

The heated raw material slurry 4 is transferred to an aging tank 8 and aged by keeping at the above-described temperature range. The reason for setting the heating temperature (aging temperature) to 250°C to 400°C is the following: At a temperature lower than 250°C, the rate of extraction of the coal 1 in the solvent 2 is decreased. At a temperature over 400°C, the coal deteriorates due to thermal decomposition, and thus the rate of extraction of the coal 1 in the solvent 2 is decreased. Also, thermal decomposition of the coal (extracted coal), which has been extracted, proceeds to accelerate the production of hydrocarbon gases such as methane, ethane, and the like, thereby decreasing the yield of the extracted coal. The aging time of the raw material slurry 5 in the aging tank 8 is 5 to 120 minutes and preferably 30 to 80 minutes.

The pressure in the aging tank 8 is preferably as high as possible for preventing evaporation of the solvent, but a recommended pressure is about 50 to 500 kPa higher than the vapor pressure of the solvent at the aging temperature (heating temperature) because a high pressure brings about an increase in equipment cost. Specifically, the pressure is about 1MPa (0.5 to 1.5 MPa) depending on the coal type and the solvent type. In the aging tank 8, the insoluble component of the coal 1 in the raw material slurry 4 is

dissolved as an extract (extracted coal) in the solvent 2,
but the insoluble component remains solid as a residual coal,
thereby maintaining a slurry state.

[Solvent removing step]: The treated slurry (referred to as
the "extracted slurry" hereinafter) 25 is transferred to a
solvent removing apparatus (solvent recovering apparatus) 12
in which the solvent is removed by evaporation to prepare a
mixture 32 as a solid mixture containing the extracted coal
and the residual coal. The extracted slurry 25 possesses
temperature and pressure, and thus the solvent is evaporated
due to the latent heat under reduced pressure. However, the
mixture 32 of the extracted coal and the residual coal
remains as a solid because it has no vapor pressure.
Therefore, vacuum distillation, spray drying, or the like
can be used for the solvent removing apparatus (solvent
recovering apparatus) 12.

The above-described treatment with the solvent causes
no thermal plasticity-expressing effect on the residual coal,
but the treatment imparts thermal plasticity to the
extracted coal due to the thermal plasticity-expressing
effect while the original coal (coal) 1 has no thermal
plasticity or lower thermal plasticity. Therefore, the
mixture 32 of the extracted coal and the residual coal has
higher thermal plasticity than that of the original coal 1
and can be used as upgraded coal for metallurgy (simply

referred to as an "upgraded coal" hereinafter).

This embodiment is disadvantageous in that it has limitation to the type of the coal used for obtaining the upgraded coal 32 for metallurgy having a predetermined thermal plasticity. However, the embodiment is advantageous in that since not only the extracted coal but also the residual coal is fully recovered and used, a sedimentation tank 9 required in second and third embodiments, which will be described below, is not required, and only one solvent removing apparatus (solvent recovering apparatus) 1 may be used, thereby decreasing the cost of equipment.

[Solvent recovering step]: The solvent 16 removed by the solvent removing apparatus (solvent recovering apparatus) 12 is preferably recycled. In other words, the solvent (circulated solvent) 16 can be passed through the heat exchanger 6 to utilize the latent heat of the solvent for preheating the raw material slurry 4 and then recycled as the solvent 2 through a solvent tank 23 and a solvent pump 24.

The organic solvent 2 used preferably comprises, as a main component, a two ring aromatic compound similar to a coal structural unit and has a boiling point of about 200°C to 300°C because the pressure in the system can be kept at about 1 MPa suitable for extraction, and the solvent 2 can be easily recovered from a liquid after extraction.

Specific examples of the organic solvent 2 include two ring

aromatic compounds such as methylnaphthalene,

dimethylnaphthalene, and naphthalene, a mixture mainly

containing any of these two ring aromatic compounds, and

carbonization oils and petroleums having boiling points in

the above-described range. The circulated solvent 16 need

not be hydrogenated for maintaining the dissolving power of

the solvent 2 as long as the solvent 12 selected as descried

above is used in treatment at the above-described

temperature and pressure. Also, the solvent 16 is not

bonded to the extracted coal to permit recovery (removal),

and thus the solvent 16 can be repeatedly used without any

problem. In addition, a small amount of oil is produced

from the coal 1 due to heat treatment in the extraction step.

The oil mainly comprises a two ring aromatic compound and

thus has the effect of supplementing the circulated solvent

16 by the self-produced oil.

[Second Embodiment]

The thermal plasticity-expressing effect cannot be

generally expected for the residual coal which is a solvent

insoluble component. Therefore, when the mixture of the

extracted coal and the residual coal after treatment with

the solvent is used directly as upgraded coal for metallurgy

as in the first embodiment, the upgraded coal may be not

sufficiently suitable for producing a reduced metal by the

carbon composite method because the thermal plasticity of the upgraded coal for metallurgy may become insufficient depending on the type of the original coal used. In this case, the extracted coal and the residual coal may be discharged separately, not as a mixture, and then proper amounts of the extracted coal and the residual coal may be mixed so as to have thermal plasticity suitable for producing the reduced metal by the carbon composite method.

Fig. 2 shows an example of a process flow of a method for producing upgraded coal for metallurgy according to another embodiment of the present invention on the basis of the above-described technical idea. In this embodiment, description of portions common to the first embodiment is omitted, and only different portions will be described. [Sedimentation step]: The extracted slurry 25 aged in the aging tank 8 is transferred to a sedimentation tank 9 and then allowed to stand for a predetermined time. As a result, the residual coal, which is a solid, gravitationally sediments at the bottom of the tank. The sedimentation time depends on the type of the coal 1, but the sedimentation time is preferably about 30 to 120 minutes. In the sedimentation, a residue sediments in an extract solution of the coal 1 in the solvent 2. The extract solution of the coal 1 in the solvent 2 can be easily continuously discharged as a supernatant 26. However, it is generally

difficult to continuously discharge only the residual coal
as the residue from the bottom of the tank. Therefore, the
residual coal is discharged as a residual coal slurry 27
containing the solvent.

[First and second solvent removing steps]: The supernatant
26 and the residual coal slurry 27 are separately discharged,
and the solvents thereof are removed by evaporation with
separate solvent removing apparatuses (solvent recovering
apparatuses) 12 and 13, respectively, to separately recover
an extracted coal 14 and a residual coal 17. Like in the
solvent recovering apparatus (solvent recovering apparatus)
12 in the first embodiment, vacuum distillation, spray
drying, or the like can be used for the solvent removing
apparatuses (solvent recovering apparatuses) 12 and 13.

[Compounding step]: The compounding ratio between the
extracted coal 14 and the residual coal 17 separately
recovered as described above is controlled to produce
upgraded coal 32 for metallurgy having desired thermal
plasticity while effectively utilizing the residual coal 17.
The compounding ratio of the residual coal 17 to the
upgraded coal 32 for metallurgy is over 0% by mass and 70%
by mass or less, preferably 60% by mass or less.

[Solvent recovering step]: Like in the first embodiment, the
solvents 15 and 16 removed by the solvent removing
apparatuses (solvent recovering apparatuses) 12 and 13,

respectively, are preferably recycled.

[Third Embodiment]

For example, when upgraded coal for metallurgy is used for producing a slag containing an oxidized nonferrous metal by the carbon composite method, mixing a slag product and coal ash decreases the product's value, and thus only an extracted coal not containing the ash is preferably used as the upgraded coal for metallurgy without being mixed with a residual coal containing the ash.

Fig. 3 shows an example of a process flow of a method for producing upgraded coal for metallurgy according to still another embodiment of the present invention on the basis of the above-described technical idea. In this embodiment, the compounding step of the second embodiment is not required, and the other portions are common to the second embodiment. Namely, in this embodiment, only the extracted coal 14 obtained from the solvent removing apparatus (solvent recovering apparatus) 12 is used as the upgraded coal 14 for metallurgy as it is, and thus a method for separately utilizing the residual coal 17 must be considered. However, the upgraded coal 14 for metallurgy having high thermal plasticity and containing no ash can be obtained.

[Fourth Embodiment]

Fig. 4 shows a step of reducing a chromium-containing

raw material used as a metal oxide raw material in a method
for producing a reduced metal by the carbon composite method
using upgraded coal for metallurgy according to a further
embodiment of the present invention. In this embodiment,
the metal oxide raw material is not limited to a raw
material containing metal oxides of Fe and Cr, and a raw
material containing metal oxide of Ni, Mn, and the like may
be used. The form of the raw material may be any one of an
ore, refining dust, and the like. Of course, the product
may be reduced iron, melted iron, melted steel; or iron
nuggets.

In Fig. 4, reference numeral 101 denotes a chromium-
containing raw material (simply referred to as a "raw
material" hereinafter) containing chromium oxide and iron
oxide; reference numeral 102, upgraded coal for metallurgy;
reference numeral 103, an agglomerator; reference numeral
104, agglomerates (mixture); reference numeral 105, a moving
hearth furnace; reference numeral 106, reduced agglomerates
(reduced mixture); reference numeral 107, a melting furnace;
reference numeral 108, a metal; and reference numeral 109, a
slag.

As the chromium-containing raw material 101, a chromium
ore or a residue in a process for producing ferrochromium,
such as dust, a slag, or the like, can be used. If required,
an iron ore or mill scales can be added to adjust the

components. When the raw material 101 contains a large amount of water, the raw material 101 is preferably previously dried. The degree of drying may be determined in view of the mixing means (the agglomerator 103 in this embodiment) used in the subsequent mixing step.

The grain sizes of the chromium-containing raw material 101 and the upgraded coal 102 for metallurgy are preferably as small as possible because the probability of contact is increased in reduction reaction, as described below. However, when the grain sizes are excessively small, granulation becomes difficult. Therefore, both the chromium-containing raw material 101 and the upgraded coal 102 for metallurgy preferably contain about 75% of grains of 200 mesh or less (75 μm or less). The chromium-containing raw material 101 and the upgraded coal 102 for metallurgy are preferably previously ground according to demand.

The compounding ratio of the upgraded coal 102 for metallurgy in the agglomerates (mixture) 104 may be determined by the amount of carbon required for reducing chromium oxide and iron oxide in the raw material 101 in the moving hearth furnace 105, the amount of carbon consumed by reduction of the residual chromium oxide in the reduced agglomerates (reduced mixture) 106 in the melting furnace 107, and the amount of carbon to be left in the metal 108. In consideration that reduction of chromium oxide is solid-
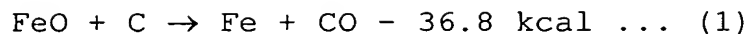
phase reaction, it is important that the amount of the
carbon compounded in the agglomerates (mixture) 104 exceeds
the theoretically required amount of carbon, which will be
described below, in order to increase the reduction rate of
chromium. Even when the compounding amount of the carbon
exceeds the theoretically required amount of carbon, the
strength of the agglomerates 104 and the reduced
agglomerates 106 is maintained due to the fact that the
improved carbon 102 for metallurgy has thermal plasticity
and functions as a binder during heating.

[Mixing step]: The raw material 101 and the upgraded coal
102 for metallurgy may be mixed using a mixer not shown in
the drawing. The resultant mixture may be charged directly
in the moving hearth furnace 105, but the mixture is
preferably agglomerated in the agglomerator 103. This is
because agglomeration decreases the amounts of the dust
produced in the moving hearth furnace 105 and the melting
furnace 107 and improves the efficiency of heat transmission
in the agglomerates (mixture) 104 to increase the reduction
rate. In particular, in the present invention, the upgraded
coal 12 for metallurgy having high thermal plasticity is
used as a carbonaceous material, and the carbonaceous
material is fluidized during heating to increase the
compactness of grains constituting the agglomerates 104,
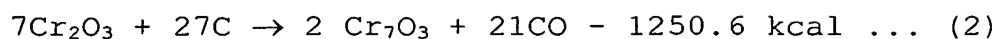thereby achieving a high efficiency of heat transmission.

The agglomerates (mixture) 104 may contain an auxiliary material such as a fluxing agent or the like. As the agglomerator 103, a compression molding machine such as a briquette press, a tumbling agglomerator such as a disk-type pelletizer, or an extrusion molding machine may be used. When the agglomerates (mixture) 104 after granulation have a high water content, the agglomerates 104 may be dried before being charged in the moving hearth furnace 105.

[Reduction step]: The agglomerates (mixture) 104 after granulation are charged in the moving hearth furnace 105 and heated by radiation. As the moving hearth furnace 105, a rotary hearth furnace, a linear furnace, a multistage furnace, or the like can be used. The radiation heating can be performed using a combustion burner or the like.

The agglomerates (mixture) 104 are rapidly heated by radiation heating, and consequently, in the agglomerates (mixture) 104, iron oxide and chromium oxide contained in the chromium-containing raw material 101 are mainly reduced by the fixed carbon contained in the carbonaceous reducing agent (upgraded coal for metallurgy) 102 according to the following reaction formulae (1) and (2) (refer to "Tekko Binran (Handbook of Iron and Steel)" edited by Iron and Steel Institute of Japan, third edition, vol. 2, Publishing Office: Iron and Steel Institute of Japan, issued on October 15, 1976):

$FeO + C \rightarrow Fe + CO - 36.8$ kcal ... (1)

$\Delta G^0 = 35350 - 35.9$ T

$7Cr_2O_3 + 27C \rightarrow 2\ Cr_7O_3 + 21CO - 1250.6$ kcal ... (2)

$\Delta G^0 = 1230132 - 886.97$ T

The reaction start temperature of formula (1) is 712°C, and the reaction start temperature of formula (2) is 1114°C. Fe produced by reaction of equation (1) is possibly partially dissolved in Cr_7O_3 produced according to equation (2) to produce $(Cr \cdot Fe)_7O_3$.

The radiation heating is preferably carried out at a mean heating rate of 13.6°C/s or more during the time from the start of the radiation heating of the agglomerates (mixture) 104 to the time when the temperature of the agglomerates (mixture) 104 reaches 1114°C, which is the reduction reaction start temperature of chromium oxide. The term "the start of the radiation heating of the agglomerates (mixture) 104" means the time when the agglomerates (mixture) 104 enter a region (radiation heating region) heated by radiation with a combustion burner or the like in the moving hearth furnace 105, excluding the time from the supply of the agglomerates (mixture) 104 onto the furnace hearth to the entrance into the radiation heating region. The reason for excluding the time from the supply of the agglomerates (mixture) 104 onto the furnace hearth to the entrance into the radiation heating region is that during

this time, the agglomerates (mixture) 104 are mainly heated only by conduction heating from the furnace hearth, and the temperature is not increased to the reduction reaction start temperature of FeO of 712°C because the retention time (passage time) is generally short, thereby causing substantially no consumption of the fixed carbon of the incorporated carbonaceous material by reduction reaction.

The atmospheric temperature of the region (reduction step) of radiation heating of the agglomerates (mixture) 104 is preferably 1250°C to 1400°C. This is because at a temperature lower than 1250°C, the heating rate of the agglomerates (mixture) 104 to 1114°C tends to become insufficient, while at a temperature over 1400°C, the reduced agglomerates (reduced mixture) 104 soften and easily bond together or adhere to the furnace hearth.

For example, when the atmospheric temperature is 1300°C, the retention time of the agglomerates (mixture) 104 in the region (reduction step) of radiation heating is preferably 5.3 to 42.7 min.

Furthermore, in order to prevent re-oxidation of Fe and Cr_7O_3 produced by reaction, the atmospheric composition of the region of radiation heating (reduction step) of the agglomerates (mixture) 104 may be a reducing atmosphere formed by controlling the air ratio of the combustion burner or blowing a reducing gas into the moving hearth furnace 105.

The reduced agglomerates (reduced mixture) 106 reduced in the moving hearth furnace 105 are generally cooled to about 1000°C by a radiation cooling plate provided in the moving hearth furnace 105 or a refrigerant spray device and then discharged by a discharge device.

The above-described theoretically required amount of carbon represents the amount of carbon theoretically required for producing $(Cr \cdot Fe)_7O_3$ through the reaction of iron oxide and chromium oxide contained in the agglomerates (mixture) 104 according to formulae (1) and (2), and defined by the following formula:

Theoretically required amount of carbon = (Number of moles of Cr_2O_3) × 27/7 + (Number of moles of O bonded to Fe) + (Number of moles of Fe) × 3/7

In the above-described reduction step, it is recommended that an atmosphere conditioning carbonaceous material is charged onto the hearth of the moving hearth furnace 105 together with the agglomerates (mixture) 104. The atmosphere conditioning material is particularly preferably charged as a bed before the agglomerates (mixture) 104 are charged onto the furnace hearth. However, even when the atmosphere conditioning material is charged simultaneously with or after charging of the agglomerates (mixture) 104, the predetermined effect can be obtained.

The effects of charging of the atmosphere conditioning

carbonaceous material are as follows:

1) The reducing atmosphere is kept near the agglomerates (mixture) 104, for preventing re-oxidation of the reduced agglomerates (reduced mixture) 106.

2) The volatile components, CO gas, and the like produced from the atmosphere conditioning material can be used as a fuel for the moving hearth furnace 105, thereby decreasing the fuel consumption of the moving hearth furnace 105.

3) Buildup on the furnace hearth can be prevented to decrease a load on a discharge device and abrasion of a member such as a blade edge or the like.

4) The atmosphere conditioning material discharged after devolatilization together with the reduced agglomerates (reduced mixture) 106 can be utilized as a reducing agent and/or a heat source in the next melting step.

As the atmosphere conditioning carbonaceous material, coal, a waste plastic, a waste tire, or a biomass is preferred. For example, when coal or biomass is used, the material is charred in the moving hearth furnace 105, and the volatile component becomes a fuel for the moving hearth furnace 105. However, the char component can be used as a reducing agent and/or a heat source of the melting furnace. Alternatively, coke, charcoal, petroleum coke, char, or the like can be used. Such a material has a low volatile

content, and thus the effect of decreasing the fuel consumption in the moving hearth furnace 105 is lower than that of coal.

The size (grain size) of the atmosphere conditioning material is not particularly limited, but a recommended average grain size is preferably 5 mm or less and more preferably 2 mm or less.

Furthermore, the thickness of the atmosphere conditioning material supplied onto the furnace hearth is preferably about 1 to 50 mm.

In addition to the atmosphere conditioning material, a hearth protecting material may be supplied for preventing build-up on the hearth. In this case, the atmosphere conditioning material is preferably charged on the hearth protecting material. As the hearth protecting material, a material containing a high-melting-point substance is preferred, and a material containing a carbonaceous substance is more preferred. As the high-melting-point substance, an oxide containing alumina and/or magnesia, or a substance containing silicon carbide is recommended. [Agglomeration step]: The reduced agglomerates (reduced mixture) 106 reduced in the reduction step may be further heated in the moving hearth furnace to agglomerate the reduced metal (Fe and Cr_7O_3) contained in the reduced agglomerates (reduced mixture) 106. The heating temperature

may be the same as or slightly higher than the temperature

in the reduction step so that the reduced metal is not

melted, and the heating time may be appropriately controlled

according to the heating temperature. In this case, the

reduced metal is agglomerated in the reduced agglomerates

(reduced mixture) 106 to increase the grain size of the

agglomerates. As a result, there are obtained the effect of

upgrading separability between the metal and the slag, as

compared with the reduced agglomerates (reduced mixture) 106

undergoing up to the reduction step without being subjected

to the agglomeration step, the effect of decreasing the

surface area of the agglomerates composed of the reduced

metal and preventing re-oxidation, and the like.

[Melting step]: The reduced agglomerates (reduced mixture)

106 discharged from the moving hearth furnace 105 are

preferably charged at a high temperature in a melting

furnace 107 without being cooled. The melting furnace 107

may be connected directly to the discharge part of the

moving hearth furnace 105 with a chute or the like, or a

conveyance device such as conveyor or a container for

storing the agglomerates 106 before charging into the

melting furnace 107 may be used. When the melting furnace

107 is not adjacent to the moving hearth furnace 105 or the

operation of the melting furnace 107 is stopped, the reduced

agglomerates (reduced mixture) 106 may be cooled to room

temperature and stored or transported as a half-finished product (ferrochromium refining raw material). Alternatively, the reduced agglomerates (reduced mixture) 106 may be hot-molded at a high temperature without being cooled, for decreasing the surface area, and the molded product may be cooled and stored or transported as a half-finished product having high resistance to re-oxidation, and then used. As the melting furnace 107, an electric furnace can be used, but a melting furnace using fossil energy such as coal, heavy oil, natural gas, or the like may also be used. If required, a fluxing material or the like is charged in the melting furnace 107, and the reduced agglomerates (reduced mixture) 106 are melted at a high temperature of 1400°C to 1700°C to separate between a metal 108 and a slag 109. The metal 108 is used directly as charge chromium or subjected to secondary refining to produce ferrochromium according to demand.

As described above, in the present invention, the compactness of the agglomerates 104 is increased by fluidization of the carbonaceous material during heating, and thus the compactness of the reduced agglomerates 106 is also increased to increase the apparent density. Therefore, the reduced agglomerates 106 can be easily immersed in a melted metal without floating on the melted metal, thereby increasing the melting speed and achieving high productivity.

[Fifth Embodiment]

Fig. 5 shows a step of reducing a chromium-containing raw material which is a metal oxide-containing raw material in a method for producing a reduced metal by the carbon composite method using an improved carbon for metallurgy according to a further embodiment of the present invention. In Fig. 5, reference numeral 111 denotes a chromium-containing raw material (simply referred to as a "raw material" hereinafter) containing chromium oxide and iron oxide; reference numeral 112, a carbonaceous reducing agent; reference numeral 113, an agglomerator; reference numeral 114, agglomerates (mixture); reference numeral 115, a moving hearth furnace; reference numeral 116, a reduced solid; reference numeral 117, a screen; reference numeral 118, a metal; and reference numeral 119, a slag.

In the fifth embodiment, the raw material 111, the carbonaceous reducing agent 112, the agglomerator 113, and the agglomerates (mixture) 114 are the same as the raw material 101, the carbonaceous reducing agent 102, the agglomerator 103, and the agglomerates (mixture) 104, respectively, in the fourth embodiment. The mixing step is also the same as in the fourth embodiment, and thus description thereof is omitted.

[Reduction and melting step]: The agglomerates (mixture) 114 produced by granulation are charged in the moving hearth

furnace 115 and heated by radiation at an atmospheric
temperature of 1250°C to 1400°C. Like in the fourth
embodiment, the mean heating rate of the agglomerates
(mixture) 114 by radiation heating may be 13.6°C/s or more
from the start of radiation heating of the agglomerates
(mixture) 114 to the time when the temperature of the
agglomerates 114 (mixture) 114 reaches the reduction
reaction start temperature of chromium oxide of 1114°C. In
this region, the retention time of the agglomerates
(mixture) 114 is preferably 5.3 to 42.7 min.

The reduced agglomerates (reduced mixture) are then
melted by heating to produce a reduced melt in the moving
hearth furnace 115 at an atmospheric temperature of 1350°C
to 1700°C, preferably 1350°C to 1650°C, and more preferably
1350°C to 1600°C, higher than the atmospheric temperature
(1250°C to 1400°C) in the reduction region. The reason for
setting the lower limit of the heat melting temperature to
1350°C is that a temperature lower than this temperature
easily causes difficulty in melting the reduced agglomerates
(reduced mixture). The reason for setting the upper limit
of the heat melting temperature to 1700°C is that a
temperature over this temperature easily causes the problem
of heat resistance of the reduction furnace. In this
temperature region, the retention time of the reduced
agglomerates (reduced mixture) may be appropriately adjusted

in a range of 0.5 to 10 min so that the reduced agglomerates (reduced mixture) are sufficiently melted to separate between a metal and a slag. The reason for setting the lower limit of the retention time of the reduced agglomerates (reduced mixture) to 0.5 min is that a retention time shorter than this easily causes insufficient separation between the metal and the slag. The reason for setting the upper limit of the retention time to 10 min is that a retention time over this brings about saturation of the degree of separation between the metal and the slag and rather increases the possibility of re-oxidation.

In the present invention, the upgraded coal for metallurgy having high thermal plasticity is used as a carbonaceous material, and thus the agglomeration property of the metal is increased to promote separation between the metal and the slag, as shown in examples which will be described below.

Instead of the above-described heating in the moving hearth furnace 115 in which the atmospheric temperature is changed in two steps, reduction and melting may be simultaneously performed by heating in one step at an atmospheric temperature of 1350°C to 1700°C from the start. In this case, the reduced melt can be obtained within a short time.

The metal and the slag are not necessarily both melted,

and only one of the metal and the slag may be melted as long
as both can be separated.

The same atmosphere conditioning material and hearth
protecting material as in the fourth embodiment can be used.
[Solidification step]: The reduced melt is solidified by
cooling to about 100°C in the moving hearth furnace 115 to
produce the reduced solid 116. As the cooling
solidification means in the moving hearth furnace 115, the
radiation cooling plate or refrigerant spray device
described in the fourth embodiment can be used. The reduced
solid 116 discharged from the moving hearth furnace 115 may
be further cooled by cooling solidification means. As the
cooling solidification means, means such as water
granulation, indirect water cooling, refrigerant spray, or
the like can be used.
[Separation step]: The reduced solid 116 is disintegrated as
occasion demands, and then screened with the screen 117 to
separate between the metal (coarse ferrochromium) 118 and
the slag 119. If required, the metal can be further
recovered from the separated slag 119 by means such as
magnetic separation, flotation, or the like. If required,
the separated metal (coarse ferrochromium) 118 is
secondarily refined to produce a ferrochromium product.
Alternatively, the metal (course ferrochromium) 118 may be
used as a half-finished product (ferrochromium refining raw

material), i.e., as a melting raw material for a melting
furnace. When the metal 118 is used as the half-finished
product, the melting energy for the slag in the melting
furnace is not required because the slag has been removed
from the metal 118 produced as the half-finished product by
the method of the fifth embodiment, and thus the energy
consumption of the melting furnace is significantly
decreased in comparison with the method of the fourth
embodiment in which the slag remains in the reduced
agglomerates produced as a half-finished product. Also, the
amount of the slag produced in the melting furnace is
significantly decreased to significantly improve the
production efficiency of the melting furnace. Furthermore,
the metal (coarse ferrochromium) 118 can be used as a raw
material for ferrochromium and can be used directly as a raw
material for producing a chromium-containing alloy.
Furthermore, the weight of the half-finished product is
decreased due to removal of the slag, and thus the storage
and transport coat can be decreased. Therefore, the present
invention is preferably carried out in a production place of
chromium ores. If required, the metal may be agglomerated
for the sake of convenience of storage and transport.

In the present invention, the metal 118 and the slag
119 are sufficiently separated in the reduction and melting
step, and thus the metal can be easily recovered in high

yield by a mechanical separation operation in the separation step.

The atmosphere conditioning material may be recovered and reused or may be charged in the melting furnace together with the metal. The hearth protecting material is preferably recovered and reused.

[Sixth embodiment]

Fig. 6 shows a step of reducing a titanium-containing raw material which is a metal oxide-containing raw material in a method for producing a slag containing an oxidized nonferrous metal by the carbon composite method using an improved carbon for metallurgy according to a further embodiment of the present invention. The metal oxide raw material is not limited to a raw material containing Fe and Ti oxides used in this embodiment, and a raw material containing metal oxides of V, Nb, and the like may be used. The form of the raw material may be any of an ore, refining dust, and the like. In Fig. 6, reference numeral 211 denotes a titanium-containing raw material (simply referred to as a "raw material" hereinafter); reference numeral 212, the upgraded coal for metallurgy; reference numeral 213, an agglomerator; reference numeral 214, agglomerates (mixture); reference numeral 215, a moving hearth furnace; reference numeral 216, a reduced solid; reference numeral 217, a screen; reference numeral 218, a metal; and reference

numeral 219, a slag.

Examples of the titanium-containing raw material 211 include, but not limited to, natural ores such as titanic magnetite, ilmenite, titanic magnetite, and pseudobrookite; and by-products in production of titanium oxide or titanium, such as a residue in a centrifugal separator and a residue after filtration in a process for producing titanium oxide by a sulfuric acid method, and a residue after chlorination by a chlorine method. The raw material may be prepared according to demand. For example, an iron ore or iron-making dust may be added for controlling the amount of iron oxide, or rutile, anatase, or synthetic rutile may be added for controlling the amount of titanium oxide. Although the raw material mixture 214 containing ilmenite as the titanium-containing raw material 211 and the upgraded coal 212 for metallurgy will be described below as a representative example, the ilmenite 211 may be a natural ore, and the ratios of titanium and iron are not particularly limited.

The ilmenite 211 generally contains 40 to 60% by mass of titanium oxide and 30 to 50% by mass of iron oxide. In order to effectively produce a titanium slag, the content of iron oxide in the raw material mixture 214 is preferably 1/20 or more and more preferably 3/20 or more of the content of titanium oxide.

The natural ilmenite 211 contains a considerable amount
of SiO_2 and the like as gangue components, but the contents
of these gangue components in the raw material mixture 214
are preferably as low as possible because the gangue
components such as Al_2O_3, CaO, MgO, and the like are mixed in
the titanium slag to decrease the titanium purity.

As the upgraded coal 212 for metallurgy, the coal of
any one of the first to third embodiments may be used, but
the coal for metallurgy of the third embodiment comprising
only the extracted coal is preferably used because the ash
is not incorporated in a slag product. The compounding
amount of the coal 212 for metallurgy in the raw material
mixture 214 is not particularly limited, but the compounding
amount is preferably controlled so that the amount of the
upgraded coal 212 for metallurgy is sufficient for reduction
of iron oxide. For example, the compounding amount is
preferably determined so that the number of the moles of
fixed carbon in the raw material mixture 214 is at least the
number of the moles of oxygen bonded as iron oxide to iron.
Since the rate of utilization of carbon depends on the raw
material and carbon, the compounding amount is preferably
appropriately controlled. The excess carbon for reduction
reaction is carburized in reduced iron and can thus be used
as carbon in pig iron. A carbonaceous reducing agent may be
charged in the furnace together with the mixture 214, or

previously placed on the hearth. In this case, the vicinity
of iron oxide can be desirably maintained in a highly
reducing atmosphere during reduction, thereby suppressing
re-oxidation of iron oxide.

[Mixing step]: The raw material mixture (agglomerates) 214
may be prepared by kneading powders of the raw material 211
and the upgraded coal 212 for metallurgy using any mixing
means (not shown in the drawing) such as a mixer or the like.
The kneading method is not particularly limited. The
resultant mixture 214 may be directly used in a power state,
but the mixture 214 is preferably formed into agglomerates
such as briquettes, pellets, plates, or the like by any
molding method such as briquette pressing, tumbling
granulation, or extrusion molding using the agglomerator 213,
for upgrading the handling property. In this embodiment,
briquette-shaped agglomerates 214 are described as a
representative example.

In producing the agglomerates 214, the agglomerates 214
are preferably mixed with an appropriate amount of a calcium
oxide source (for example, calcium hydroxide, calcium oxide,
or the like), for controlling the composition of titanium
slag components (titanium oxide, the gangue components in
the ore used as the raw material, and the slag components
contained as ashes in the carbonaceous material, such as
SiO_2, Al_2O_3 and CaO) contained in the agglomerates 214. In

this case, the melting point of the titanium slag produced
in melting of the reduced iron is desirably decreased, and
the thermal plasticity of the titanium slag is increased,
thereby increasing separability between the titanium slag
and the melted iron. For example, the agglomerates 214
containing calcium oxide may be produced by granulation or
the agglomerates 214 may be covered with a calcium oxide
source and then oxidized so that the calcium oxide source is
present during melting.

In granulation to produce the agglomerates 214,
bentonite, starch, calcium hydroxide, or a binder such as an
organic binding agent may be used according to demand.
[Reduction and melting step]: The moving hearth furnace 215
used in the present invention is not limited as long as it
includes a moving-type hearth. For example, any structure
furnace such as a straight grate type or a rotary hearth
furnace can be used.

The moving hearth furnace 215 is preferred because the
temperature is easily controlled, and iron oxide can be
selectively reduced with high efficiency within a short time
at a lower temperature than that in a conventional electric
furnace, i.e., a temperature lower than the reduction start
temperature of titanium oxide. In particular, the rotary
hearth furnace is preferred because the equipment has a
relatively small unnecessary space, the atmosphere in the

furnace can be easily controlled, and the reduction rate of iron oxide can be increased while suppressing reduction of titanium dioxide.

Description will be made of use of the rotary hearth furnace as the moving hearth furnace 215 as a representative example, but the method of the present invention does not have the view that the moving hearth furnace 215 is limited to the rotary hearth furnace.

Reduction is preferably performed in the furnace at a temperature kept in a range of 1200°C to 1500°C and more preferably 1200°C to 1400°C. This is because within the range of 1200°C to 1500°C, only iron oxide can be selectively reduced with high efficiency without reduction of titanium oxide.

At a heating temperature lower than 1200°C, reduction reaction of iron oxide slowly proceeds, and thus the retention time in the furnace must be increased to lower productivity. On the other hand, at a furnace temperature exceeding 1500°C, reduction reaction of titanium oxide proceeds to decrease the recovery rate of the titanium slag. Also, at a temperature over 1500°C, a low-melting-point slag containing FeO bleeds out during reduction, and the dissolution loss of the hearth refractory becomes significant, thereby causing difficulty in a continuous operation. Although bleeding may occur in the temperature

range of 1400°C to 1500°C depending on the composition and
compounding amount of the agglomerates, the frequency and
possibility of bleeding are relatively low. Therefore, the
temperature in the reduction period is preferably in a range
of 1200°C to 1500°C and more preferably 1200°C to 1400°C.
In an actual operation, of course, the temperature in the
furnace may be set to 1200°C or less in the early stage of
the reduction period and then increased to 1200°C to 1500°C
for promoting reduction.

The reduction of iron oxide can be generally completed
within about 5 to 20 minutes slightly depending on the ratio
between iron oxide and titanium oxide which constitute the
agglomerates 214 and the type of the carbonaceous material
(upgraded coal for metallurgy).

The above-described reduction of the mixture
(agglomerates) 214 produces a reduced mixture in which iron
oxide is mostly reduced to metallic iron, but titanium oxide
is hardly reduced.

Then, the temperature in the furnace is increased to
1300°C to 1500°C, for reducing the remaining iron oxide and
melting the produced reduced iron. By using this two-stage
heating method, both the metallic iron and titanium oxide
can be stably produced with high efficiency. Therefore,
when the two-stage heating method is used, the rotary hearth
furnace desirably has a structure in which the inside is

divided into at least two sections using partitions in the
moving direction of the furnace so that the section on the
upstream side can be used as a reduction section, the
section on the downstream side can be used as a heat-melting
section, and the temperatures and atmospheric gas
compositions of these sections can be separately controlled.
The inside of the furnace may be divided into at least three
sections using two or more partitions so that the
temperatures and atmospheric gas compositions can be more
strictly controlled. The number of the divided sections can
be randomly changed according to the scale and structure of
the moving hearth furnace.

In order to smoothly and efficiently promote the
reduction and melting, the melting temperature in the
furnace is preferably set to be about 100 to 300°C and more
preferably 120 to 250°C higher than the reduction
temperature.

The titanium slag is not necessarily melted. When the
discharged product is recovered as a mixture of the iron
nuggets 218 and the slag grains 219, the mixture discharged
from the furnace is crushed and then screened by any desired
means such as magnetic separation or the like to obtain the
titanium-containing slag 219, as described in the separation
and recovery step below. In the present invention, the
upgraded coal 212 for metallurgy having high thermal

plasticity is used as the carbonaceous material, and thus the agglomeration property of the melted iron can be increased, thereby facilitating separation between the iron nuggets 218 and the slag granules 219. Also, the metallic iron is little mixed in the slag grains to produce the titanium-containing slag 219 of high quality.

[Solidification step]: When a cooling portion provided with any cooling means is further provided in the furnace, the melted iron is cooled and solidified to produce the reduced solid 216, and thus the reduced solid 216 can be easily scraped out from the furnace using a discharge device provided on the downstream side.

[Separation and recovery step]: The reduced solid 216 is disintegrated as occasion demands, and then sieved with the screen 217. Furthermore, if required, the metal (iron nuggets) 218 and the slag (slag grains) 219 are separated by magnetic separation or the like (not shown) to obtain the titanium slag 219 of high quality.

EXAMPLES

The present invention will be described in detail below with reference to examples, but the present invention is not limited to these examples, and proper modifications can be made within a range suitable for the above- and below-described view of the invention. These modifications are

also included in the technical field of the present
invention.

[EXAMPLE 1]

The two types of coal shown in Table 1 were treated
with a bicyclic organic solvent, 1-methylnaphthalne, at each
of the extraction temperatures (heating temperatures) and
each of the extraction times (aging times) shown in Table 2.
As a result, extracted coal and residual coal were obtained
in the yields shown in Table 2.

Table 1

Coal type	Class	Composition (% by mass, dry base)						Thermal plastic-ity
		Ash	Carbon	Oxygen	Nitrogen	Sulfur	Volatile	
Coal 1	Sub-bituminous coal	11.6	69.2	5.0	1.7	1.3	41.5	No
Coal 2	Bituminous coal	10.3	78.9	4.9	2.1	0.6	28.8	Yes

Table 2

Coal type	Extraction temperature (°C)	Extraction time (min)	Yield (% by mass)			
			Extracted coal	Residual coal	Oil + water	Gas
Coal 1	400	40	41.8	54.5	2.3	1.4
Coal 2	300	60	61.7	35.8	1.5	1.0

The extracted coal and the residual coal obtained by

solvent treatment of coal 1 (sub-bituminous coal, high-volatile coal) shown in Table 1 were mixed at various compounding ratios to prepare upgraded coals. The Gieseler thermal plasticity test of the upgraded coals produced the results shown in Table 8. Table 8 indicates that by using the method of the present invention, coal initially showing no thermal plasticity can be upgraded to coal exhibiting thermal plasticity, and thermal plasticity can be changed by controlling the compounding ratio between the extracted coal and the residual coal.

Table 3

Test No.	Compounding ratio of residual coal (% by mass)	Thermal plasticity start point (°C)	Maximum thermal plasticity log(MFD)	Thermal plasticity
1	0 (only extracted coal)	275	> 4.8	very high
2	50	176	> 4.8	very high
3	58	215	1	high

Also, upgraded coal was obtained from coal 1 only by heat treatment (400°C) in a solvent without separation between extracted coal and residual coal. This upgraded coal exhibited the thermal plasticity as shown in Table 4.

Table 4

Test No.	Compounding ratio of residual coal (% by mass)	Thermal plasticity start point (°C)	Maximum thermal plasticity log(MFD)	Thermal plasticity
4	No separation operation	275	0.5	some

Table 4 indicates that coal without thermal plasticity can be upgraded to coal having thermal plasticity by heat treatment with a solvent without a separation operation. However, it is found that when the coal is separated into extracted coal and residual coat (Test No. 3 in Table 3), the thermal plasticity is more improved as compared with a case (Test No. 4 in Table 4) in which only heat treatment is performed under the same conditions. This is possibly due to the fact that even when the agglomeration of coal molecules is relieved by heating to extract a component having thermal plasticity, coexistence of the component of the residual coal causes re-agglomeration with the component molecules of the residual coal having no thermal plasticity due to cooling or polymerization of part of pyrolytic radicals with the residual coal to stabilize the radicals, thereby decreasing the thermal plasticity in comparison with the case in which the separation operation is performed. Therefore, in order to obtain higher thermal plasticity or control the ash content and thermal plasticity of the

upgraded coal, it is desirable to use the method of separating between the extracted coal and the residual coal and then properly controlling the compounding ratio of the residual coal.

It was also confirmed that with coal 2 initially having thermal plasticity, the extracted coal exhibited higher thermal plasticity. However, the residual coals of both coals 1 and 2 did not exhibit thermal plasticity.

[EXAMPLE 2]

Each of coal 1 and coal 2 was treated with a bicyclic aromatic solvent, 1-methylnaphthalene, which was used in EXAMPLE 1, for a constant extraction time (aging time) of 40 minutes at changing extraction temperatures (heating temperatures). Fig. 7 shows the relation between the extraction temperature and the extraction rate of coal. As shown in Fig. 7, the coal dissolves out at about 200°C, and the extraction rate increases with the temperature. However, the extraction rate conversely decreases at a predetermined temperature or more. This is due to the fact that pyrolysis of the coal vigorously occurs, and the molecules become larger than the initial molecules due to polymerization reaction of pyrolytic molecules or the like. Therefore, heating is preferably performed under appropriate conditions at an optimum temperature for each coal type. The results of a test using many types of coal show that the heat

treatment temperature is preferably about 350°C to 420°C.
[EXAMPLE 3]

Each of coal 1 and coal 2 was treated with a bicyclic aromatic solvent, 1-methylnaphthalene, which was used in EXAMPLE 1, at a constant extraction temperature (heating temperature) for changing extraction times (aging times). Fig. 8 shows the relation between the extraction time and the extraction rate of coal. As shown in Fig. 8, the extraction rate is substantially constant and shows a saturated state with an extraction time of about 40 to 120 minutes regardless of the extraction temperature. However, it is found that at an extraction temperature of as high as 420°C, the adequate extraction time is about 10 minutes.
[EXAMPLE 4]

Coal 1 was repeatedly extracted using, as an initial solvent, a bicyclic aromatic solvent, 1-methylnaphthalene, which was used in EXAMPLE 1, and the solvent was repeatedly recovered. Fig. 9 shows the relation between the number of repeated uses and the extraction rate of coal. Fig. 9 indicates that even when the solvent is repeatedly used, the extraction rate is substantially constant, and thus the bicyclic aromatic solvent can be stably recycled.
[EXAMPLE 5]

A reduction test simulating production of a reduced metal (reduced iron) by the carbon composite method was

carried out. An iron ore was used as a metal oxide, and the following three types of carbonaceous materials were used: (1) high-volatile coal (coal 1) not treated with a solvent, (2) upgraded coal (Test No. 4 in EXAMPLE 1) obtained only by solvent treatment of the high-volatile coal (coal 1) without separation between extracted coal and residual coal, (3) upgraded coal (Test No. 3 in EXAMPLE 1) obtained by solvent treatment of the high-volatile coal (coal 1), separating between extracted coal and residual coal, and then again mixing the extracted coal and the residual coal at the same ratio as that in the separation operation. Tables 8 to 10 show the compositions and grain sizes of the iron ore and carbonaceous materials used in this example. The iron ore was mixed with each carbonaceous material to prepare a mixed raw material, and 5 g of the mixed raw material was charged in a cylinder of 20 mm in diameter. Then, a load of 20 ton was applied to form a tablet, and the formed tablet was reduced at 1300°C in a nitrogen atmosphere in a small heating furnace. The compounding ratio of the carbonaceous material in the mixed raw material was adjusted so that the amount of the residual carbon in reduced iron was 6% by mass.

Table 5 shows the crushing strength of the reduced iron obtained by the reduction test. As shown in Table 5, when coal 1 (high-volatile coal) without thermal plasticity is used, the strength of the reduced iron becomes very low

(Test No. 1-1), while when coal 1 (high-volatile coal) initially having no thermal plasticity is upgraded by solvent treatment, a soft melting property is exhibited. It is also found that by using such upgraded coal as a carbonaceous material to be incorporated, the strength of reduced iron is significantly improved (Test Nos. 1-2 and 1-3). The yield of the upgraded coal from original coal 1 (high-volatile coal) was 96%, and the degrees of metallization of reduced iron in all tests were about 90%.

Table 5

Test No.	Type of carbonaceous material	Gieseler maximum thermal plasticity of carbonaceous material log(MFD)	Crushing strength of reduced iron (N/piece of DRI)	Evaluation	Remarks
1-1	High-volatile coal (unupgraded coal)	0	25	Bad	Comparative example
1-2	Upgraded coal (no separation operation)	0.5	118	Good	Example of this invention
1-3	Upgraded coal (prepared by re-mixing after separation operation)	1	157	Excellent	Example of this invention

[EXAMPLE 6]

Unlike in EXAMPLE 5, a reduction test was carried out under conditions in which the reduction temperature was

increased to 1450°C to melt and separate between a metal and a slag. The compounding ratio of a carbonaceous material in a mixed raw material was adjusted so that the amount of the residual carbon in the metal (iron nuggets) was 4.5% by mass.

A metal produced by the reduction test was cooled to obtain a solid, and the resultant solid was disintegrated then separated into iron nuggets (metal) and a slag by magnetic separation. Table 6 shows the ratio of the iron nuggets with a grain size of 0.5 mm or more in the iron nuggets recovered after separation. As shown in Table 6, when coal 1 (high-volatile coal) without thermal plasticity is used, the obtained iron nuggets mainly comprise grains with a grain size of 0.5 mm or less (Test No. 2-1), while when the upgraded coal having thermal plasticity is used, the ratio of grains of 0.5 mm or less is significantly decreased, and the iron nuggets mainly comprise grains of 0.5 mm or more (Test Nos. 2-2 and 2-3). This is possibly due to the fact that when the coal is upgraded by solvent treatment, the thermal plasticity are improved, and the use of such upgraded coal as a carbonaceous material to be incorporated improves the agglomeration property of melted iron and increases the grain size of the iron nuggets. When coal 1 (high-volatile coal) was used (Test No. 2-1), the yield of the upgraded coal from the original coal was 96%, while when coal 2 (bituminous coal) was used (Test No. 2-3),

the yield was 97%.   In all tests, the rates of metallization of iron nuggets were about 100%.

Table 6

Test No.	Type of carbonaceous material	Gieseler maximum thermal plasticity of carbonaceous material log(MFD)	Ratio of grains of +0.5 mm in iron nuggets (% by mass)	Evaluation	Remarks
2-1	High-volatile coal (unupgraded coal)	0	3	Bad	Comparative example
2-2	Upgraded coal of high-volatile coal (no separation operation)	0.5	70	Good	Example of this invention
2-3	Upgraded coal of bituminous coal (no separation operation)	4	98	Excellent	Example of this invention

[EXAMPLE 7]

A reduction test simulating production of a slag (titanium oxide slag) containing an oxidized nonferrous metal by the carbon composite method was carried out.   As a metal oxide, ilmenite was used, and the following three types of carbonaceous materials were used: (1) bituminous coal (coal 2) not treated with a solvent, (2) an extracted coal produced by solvent treatment of bituminous coal (coal 2), and (3) an extracted coal (Test No. 1 in EXAMPLE 1) produced by solvent treatment of high-volatile coal (coal 1).

When the carbonaceous material (2) was used, the carbonaceous material was mixed only with the ilmenite to prepare a mixed raw material. In addition, calcium oxide was further added to a mixed raw material so that the ratio CaO/SiO_2 of a slag composition was 0.4, and a FeO reagent was further added to a mixed raw material so that the total Fe content in the mixed raw material was 40% by mass. These prepared mixed raw materials were used in the reduction test. Tables 8 to 10 show the component compositions and grain sizes of the ilmenite and each carbonaceous material used in this embodiment. The ilmenite iron ore was mixed with each carbonaceous material to prepare the mixed raw material, and 5 g of the mixed raw material was charged in a cylinder of 20 mm in diameter. Then, a load of 20 ton was applied to form a tablet, and the formed tablet was reduced at 1500°C in a nitrogen atmosphere in a small heating furnace. The compounding ratio of the carbonaceous material in each mixed raw material was adjusted so that the amount of the residual carbon in the metal (iron nuggets) was 2% by mass.

A melt produced by the reduction test was cooled to obtain a solid, and the resultant solid was disintegrated and then separated into iron nuggets (metal) and a slag by magnetic separation. Table 7 shows the ratio of the iron nuggets with a grain size of 0.5 mm or more recovered after separation, and the component composition of the slag.

When coal 2 (bituminous coal) initially having a certain degree of thermal plasticity but not treated with the solvent is used, the obtained iron nuggets mainly comprise grains with a grain size of 0.5 mm or less (Test No. 3-1), while when the upgraded coal having significantly improved thermal plasticity is used, the ratio of grains of 0.5 mm or less is significantly decreased, and the iron nuggets mainly comprise grains of 0.5 mm or more (Test Nos. 3-2 to 3-5). In particular, when the basicity of the slag is controlled by adding calcium oxide (Test No. 3-4), the TiO_2 purity in the slag is slightly decreased, but not only the metal but also the slag is melted during reduction to facilitate agglomeration of the metal, thereby significantly increasing the ratio of the grains of 0.5 mm or more in the iron nuggets. When the iron content in the mixed raw material is increased by adding the FeO reagent (Test No. 3-5), the slag is little melted during reduction, and thus the agglomeration effect of the metal is lower than that with the raw material (Test No. 3-4) having the controlled basicity. However, agglomeration of the metal is accelerated by increasing the amount of the metal (melted iron), and thus the ratio of the grains of 0.5 mm or more in the iron nuggets is slightly increased. In this case, the TiO_2 purity in the slag is not decreased.

When the extracted coal having no ash is used as the

upgraded coal (Test No. 3-2 to 3-5), the ratio (TiO_2 purity) of the TiO_2 component in the slag is increased, as compared with the use of the high-volatile coal having ash (Test No. 3-1).

When the upgraded coal (extracted coal) obtained from high-volatile coal is used (Test No. 3-3), the volatile content of the extracted coal is increased, and the amount of fixed carbon contributing to reduction and carburization is small. Therefore, the amount of the necessary carbonaceous material is larger than that in use of the upgraded coal (extracted coal) of bituminous coal (Test No. 3-2, 3-4, and 3-5).

When the high-volatile coal was used (Test No. 3-2), the yield of the upgraded coal (extracted coal) from the original coal was 62%, while when bituminous coal was used (Test Nos. 3-3 to 3-5), the yield was 42%. In all tests, the rates of metallization of iron nuggets were about 100%.

Table 7

Test No.		3-1	3-2	3-3	3-4	3-5
Type of carbonaceous material		Bituminous coal (unupgraded)	Upgraded coal of bituminous coal (extracted coal)	Upgraded coal of high-volatile coal (extracted coal)	The same as the left	The same as the left
Gieseler maximum thermal plasticity of carbonaceous material log(MFD)		3 .	>4.8	>4.8	>4.8	>4.8
Other additive		No	No	No	Calcium oxide	FeO
Ratio of grains of +0.5 mm in iron nuggets (% by mass)		50	90	82	99	92
Slag component % by mass	TiO_2	79.2	79.2	82.2	80.6	82.4
	FeO	0.8	0.8	0.8	0.8	0.8
	SiO_2	8.4	8.4	6.0	5.9	5.9
	Al_2O_3	2.3	2.3	1.3	1.3	1.3
	CaO	0.5	0.5	0.5	2.4	0.5
	MgO	8.3	8.3	8.7	8.5	8.7
Evaluation		Bad	Excellent	Good	Excellent	Excellent
Remarks		Comparative Example	Example of this invention	Example of this invention	Example of this invention	Example of this invention

Table 8

Type of carbonaceous material		Coal 1 (high-volatile coal)	Coal treated with solvent (no separation)	Extracted coal	Residual coal
Volatile matter content		41.5	36.4	60.4	18.0
Fixed carbon content		46.9	51.3	39.55	60.3
Ash content		11.6	12.3	0.05	21.7
Ash composition % by mass	SiO_2	62.4	–	–	62.4
	Al_2O_3	25.7	–	–	25.7
	CaO	0.2	–	–	0.2
	MgO	0.2	–	–	0.2
	Fe_2O_3	8.7	–	–	8.7
	TiO_2	2.0	–	–	2.0

Table 9

Type of carbonaceous material		Coal 1 (bituminous coal)	Coal treated with solvent (no separation)	Extracted coal	Residual coal
Volatile matter content		33.1	32.6	38.8	23.7
Fixed carbon content		56.6	57.1	61.18	60.3
Ash content		10.3	10.3	0.02	16.0
Ash composition % by mass	SiO_2	48.4	–	–	48.4
	Al_2O_3	26.1	–	–	26.1
	CaO	0.9	–	–	0.9
	MgO	0.1	–	–	0.1
	Fe_2O_3	7.6	–	–	7.6
	TiO_2	2.0	–	–	2.0

Table 10

Type of raw material		Iron ore	Titanium ore	Calcium oxide	FeO reagent
Grain size		<75 μm, 80%	<75 μm, 80%	–	–
Composition % by mass	T.Fe	68.0	34.8	0.3	76.0
	FeO	0.1	32.3	–	99
	Fe_2O_3	97.1	13.9	0.4	–
	SiO_2	1.1	3.3	6.8	0.8
	Al_2O_3	0.5	0.7	2.1	0.2
	CaO	0.4	0.3	88.9	–
	MgO	0.1	4.7	1.4	–
	TiO_2	0.0	44.5	0.0	–

Industrial Applicability

As described in detail above, the present invention can provide a method for upgrading low rank-coal such as high-volatile coal, which is unsuitable for a conventional carbon composite method, to produce upgraded coal for metallurgy suitable for the carbon composite method. Also, the present invention can provide a method for producing a high-quality reduced metal and slag containing an oxidized nonferrous metal using such upgraded coal for metallurgy.